The Detection of Unstable Molecules by Microwave Spectroscopy: Phospha-alkenes CF_2=PH, CH_2=PCl, and CH_2=PH†

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Summary The unstable phospha-alkenes CF_2=PH, CH_2=PCl, and CH_2=PH have been identified by microwave spectroscopy as products in the pyrolysis of CF_3PH_2, CH_3PCl_2, and $(CH_3)_2PH$, respectively.

ELEMENTS in the second row of the Periodic Table show a well known reluctance to form stable compounds in which they are components in a *pπ–pπ* multiple bond. For example, in the case of sulphur the aliphatic thiocarbonyls and thioaldehydes readily polymerise to thianes[1] unless the attached groups are bulky or fluorinated.[2] While phosphabenzene derivatives are stable,[3] the only characterised trivalent phosphorus compound containing an isolated multiple bond is HC≡P[4] which has only limited stability in

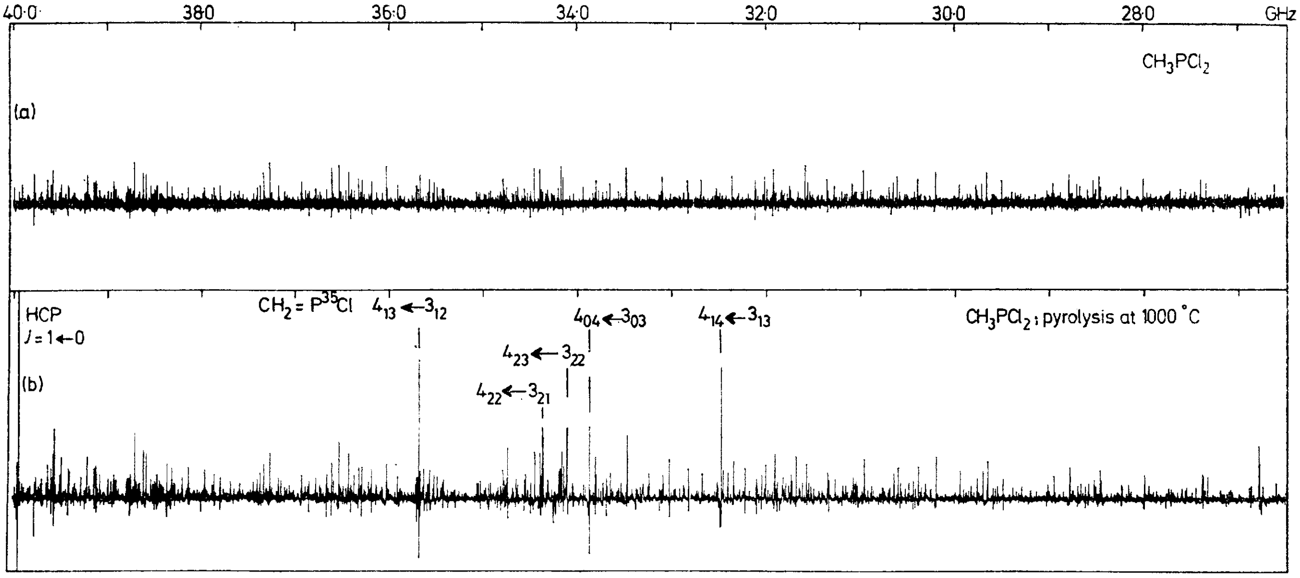

FIGURE. (a) Wide-band scan of the microwave spectrum of CH_3PCl_2. (b) Wide-band scan of the spectra obtained when CH_3PCl_2 is pyrolysed at 1000 °C. The strong new lines between 32·5 and 35·7 MHz belong to the $J=4\leftarrow3$ transitions of $CH_2=P^{35}Cl$. The strong line near 40 GHz belongs to HC≡P.

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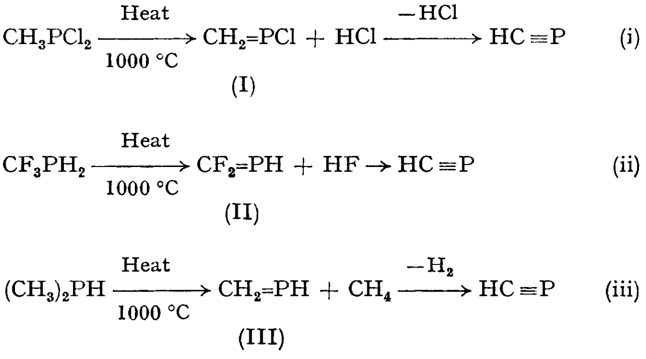
† No reprints available.

the condensed phase at very low temperature. Molecules containing *pπ–pπ* bonded silicon have been postulated to have transient existence, mainly on the basis of chemical trapping experiments.[5]

Pyrolysis techniques have been developed to produce several sulphur and selenium doubly bonded species in low pressure (10—30 μmHg) flow systems where their lifetimes are of the order of a few seconds. Using microwave and/or photoelectron spectroscopy such species as H_2CS,[6] CH_3CHS,[7] CH_3CHSe,[8] H_2CCS,[9] and HBS[10] have been identified and studied in detail.

We now report the extension of his approach to the study of some simple molecules in which trivalent phosphorus is bound to carbon by a double bond (see Scheme). These new phospha-alkene species (I), (II), and (III) have been detected by microwave spectroscopy and are phosphorus analogues of methanimine, $CH_2{=}NH$. The fluorinated species, $CF_2{=}PH$ (II) has been previously postulated as a reaction intermediate[11] and its ion detected in the mass spectra of certain stable trifluoromethyl phosphines.[12]



$$CH_3PCl_2 \xrightarrow[1000\,^{\circ}C]{\text{Heat}} \underset{(I)}{CH_2{=}PCl} + HCl \xrightarrow{-HCl} HC{\equiv}P \qquad (i)$$

$$CF_3PH_2 \xrightarrow[1000\,^{\circ}C]{\text{Heat}} \underset{(II)}{CF_2{=}PH} + HF \rightarrow HC{\equiv}P \qquad (ii)$$

$$(CH_3)_2PH \xrightarrow[1000\,^{\circ}C]{\text{Heat}} \underset{(III)}{CH_2{=}PH} + CH_4 \xrightarrow{-H_2} HC{\equiv}P \qquad (iii)$$

Scheme

Differing amounts of $HC{\equiv}P$ have also been detected in these experiments as indicated in the Scheme. In (i) the new compound (I) is clearly an intermediate in the reaction previously reported by Gier[4] in which CH_3PCl_2 is formed by the addition of HCl to $HC{\equiv}P$. The microwave line of $HC{\equiv}{}^{13}P$ is detected most strongly in this system. In (ii) the identification of $HC{\equiv}P$ clearly indicates that an atom transfer reaction of hydrogen from phosphorus to carbon has taken place.

In the Figure (a), a wide-band microwave spectrum of the parent species in the Scheme (i), CH_3PCl_2, is depicted. On pyrolysis at 1000 °C the parent spectrum is still quite strong but several very strong new lines appear as shown in the Figure (b). These new features have the correct pattern and lie very close to the frequencies predicted previously on the basis of an initial assumed structure for the species $CH_2{=}P^{35}Cl$. The more prominent $J = 4 \leftarrow 3$ transitions are assigned in the Figure (b). Each of the new features shows quadrupole hyperfine structure consistent with that expected for a molecule containing a single spin $^3/_2$ chlorine nucleus.[14] The spectrum belonging to the less abundant species, $CH_2{=}P^{37}Cl$, has also been detected.

Analogous results are obtained when CF_3PH_2 is pyrolysed in that a new spectrum is readily detected entirely consistent with that expected for the species $CF_2{=}PH$. In the case of $CH_2{=}PH$, only one transition, the $J = 1 \leftarrow 0$ line, has been detected and assigned on the basis of its characteristic Stark pattern and the proximity with which its frequency was predicted. Further work on this species will require microwave equipment operating above 60 GHz.

Half-lives of 1·5 and 1·3 min were determined for $CH_2{=}PCl$ and $CF_2{=}PH$, respectively, by stopping the flow through the cell and measuring the rate of disappearance of the absorptions in a static system. Under our conditions we found $HC{\equiv}P$ showed no diminution in its transition intensity during 3 min.

Table. Observed rotational constants, calculated constants, and preliminary structural data on which the calculated constants are based.

	$CH_2{=}PCl$		$CF_2{=}PH$		$CH_2{=}PH$	
	obs.	calc.	obs.	calc.	obs.	calc.
A_0	22 711·17	22 749·2	11 107·33	11 402·9	—	139 424·8 MHz
B_0	4 667·23	4 663·1	4 766·37	4 745·8	—	16 395·4 MHz
C_0	3 865·45	3 869·9	3 330·79	3 351·1	—	14 670·3 MHz
B_0+C_0	8 532·68	8 533·0	8 097·17	8 096·9	31 067·12	31 065·7 MHz
	r(C–H)	1·09[a]	r(C–F)	1·315[c]	r(C–H)	1·09[a] Å
	r(C=P)	1·670	r(C=P)	1·671	r(C=P)	1·670 Å
	r(P–Cl)	2·04[b]	r(P–H)	1·420[d]	r(P–H)	1·420[d] Å
	∠H–C–H	117°[a]	∠F–C–F	107°[c]	∠H–C–H	117°[a]
	∠C–P–Cl	104·5°	∠C–P–H	100°	∠C–P–H	100°

[a] From $CH_2{=}NH$, ref. 16. [b] From PCl_3, ref. 17. [c] From $F_2C{=}S$, ref. 18. [d] From $(CH_3)_2PH$, ref. 15.

The observed values of the rotational constants A_0, B_0, and C_0 for $CH_2{=}PCl$ and $CF_2{=}PH$ are given in the Table as well as the value of B_0+C_0 for $CH_2{=}PH$. Also given are the rotational constants derived from sets of preliminary structural data. Several structural parameters, other than the C=P bond length and the angle at phosphorus, have been transferred from other known species. The C=P bond length and the angle at phosphorus were then varied to give good agreement both with the observed rotational constants and among themselves. The structures used are expected to be quite close to those finally to be derived but are presented here only as evidence for the correct identification of the new species. The C≡P bond length in HC≡P is 1·5421 Å[13] and the C–P bond length in $(CH_3)_2PH$ is 1·848 Å.[15] The preliminary value of the C=P bond length in the phospha-alkenes is 1·67 Å, clearly close to that expected.

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